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Investigation of Organic Semiconductor
for Photovoltaic Application

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13. ABSTRACT 1) Based on photovoltaic current-voltage measurement, cells of tetracene with a TCNQ layer are found to have 50 times improved efficiency. Further improvement can be made by reducing the shunt conductivity. 2) Transient photovoltaic effect shows a decay under a continuous photoexcitation as well as a repeated excitation, indicating an exhaustion of the photoionization centers. 3) Transient effect under different wavelength light indicates a simultaneous presence of positive and negative currents. The magnitudes of these currents are almost equal at a given wavelength. Therefore, the net difference, i.e. the steady state signal, is more than one order of magnitude smaller than the individual current. 4) Two new solar cell configurations are proposed--(i) to use flexible substrate and to use an evaporated silicon oxide layer on the top of the cell for light entrance; (ii) According to (3), major current is from the surface recombination, therefore, a cell with repeated layer structure is suggested.		

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Abstract

Four problems are discussed concerning the photovoltaic properties of tetracene and other organic material solar cells:

(1) Based on photovoltaic current-voltage measurement, cells of tetracene with a TCNQ layer are found to have about 50 times improved efficiency. This mixed layer type cell has a shunt conductance and further improvement can be made by reducing the conductivity.

(2) Transient photovoltaic effect has been measured which shows a decay under continuous photoexcitation. This current also decreases under a repeated excitation and indicates an exhaustion of the photoionization centers.

(3) Transient effect measured with different wavelength light indicates a simultaneous presence of both positive and negative currents. The magnitudes of these currents are almost equal at each wavelength---independent of the wavelengths. Therefore, the resultant net difference, which gives the steady state signal, is more than one order of magnitude smaller than the individual current.

(4) Two solar cell configurations are proposed: (i), to use flexible substrate and to replace the quartz window light entrance by silicon oxide on the opposite side of the substrate; (ii), according to (3), a major current is contributed by the surface recombination, therefore, a cell with repeated layer structure is suggested.

Index

Abstract

I.	Introduction	1
II.	Photovoltaic Current Voltage Curve	2
III.	Transient Photovoltaic Effects in Tetracene	4
IV.	Spectral Response of Transient Photovoltaic Currents	10
V.	Solar Cell Configurations.	12
VI.	(1) References	14
	(2) Contributing personnel	15
	(3) Appendix I	
	(4) Appendix II	

List of Figures

- Fig. 1. Photovoltaic current-voltage curves of three types of organic material solar cells.
- Fig. 2. Photovoltaic current-voltage curves of silicon solar cells shunted by different resistors.
- Fig. 3 Shape of light pulses, (a) with direct electrical light switch, (b) with mechanical shutter. (Zero light level is indicated by an arrow on upper right corner.)
- Fig. 4. Transient response of tetracene solar cell (a) and silicon solar cell reference (b).
- Fig. 5. Same as Fig. 4 except at different time scale.
- Fig. 6. A "fatigue" of the transient response due to repeated excitations.
- Fig. 7. Detailed initial response curve, (a) silicon, (b) tetracene.
- Fig. 8. A "recovery" of the transient response due to interrupted excitation.
- Fig. 9. Semi-log plot of the recovery rate curve.
- Fig. 10 Same as Fig. 9 except with $6k\Omega$ instead of $1M\Omega$ shunt.
- Fig. 11 Transient photovoltaic current of "Pyrazine 101" TCNQ cell.
- Fig. 12 Photovoltaic current-voltage curves of a tetracene cell under direct light illumination (open) and under the light (covered) by another similar cell.

I. Introduction

The objective of this research is three-fold:

- (1) To perform measurements associated with the photovoltaic properties of solar cells made with organic semiconductor materials,
- (2) to analyze the measured results in terms of physical process involved in the production of the photovoltaic current, and
- (3) to utilize the analyzed results to design methods for an improvement of the energy conversion efficiency of the solar cells.

Most of the experimental work and the theoretical analysis in this investigation have been concentrated on tetracene, some new materials have been studied only in a cursory manner. However, the methods developed for the present investigation are equally applicable to most other organic semiconductors.

In Section II of this report, a new photovoltaic current-voltage measurement system is used to evaluate three types of solar cells of different organic semiconductor configurations. In Section III, transient photovoltaic current of organic solar cells under white light is investigated. The same current under a selected wavelength of light is investigated in Section IV. Finally, in Section V, some new organic solar cell configurations are proposed.

II. Photovoltaic Current-Voltage Curve

(1) Experimental Results

In the previous report¹⁾ we have described a system for the photovoltaic current-voltage (i-v) measurement. Organic semiconductors have generally very high impedance (~ 10 to $100^4 \Omega$) and a long relaxation time (in the order of seconds) to reach a steady state. Therefore, we have had to take data at discrete points: to wait at each point until a steady state is reached before proceeding to the next point.

Through the theoretical studies, which will be presented in Part B, we found that the relaxation time is dependent on the condition of light excitation: the condition to reach the steady state is faster if the variation of excitation condition is gradual. This result suggests that we build a slow motor driving system to vary continuously a variable voltage source. This voltage is used to compensate for the photovoltaic voltage of the specimen in variable load conditions. In this way a continuous i-v curve is obtained. The time it takes to measure an i-v curve is about 9 minutes.

With the above arrangement three types of specimens are measured:

Type (A), tetracene with Al as one electrode, adjacent to the glass substrate, and Au as the other electrode.

Type (B1), double layer consists of 1.5μ of TCNQ and $600-700 \text{ \AA}$ of tetracene, with Au for both electrodes and the order of layers are glass Au tetracene-TCNQ-Au.

Type (B2), same as (B1) in organic semiconductor, but with different electrodes, the order of layers are, glass-Al-tetracene-TCNQ-Au.

The respective i-v curves are shown in Fig. 1. The curves have rather unique characteristics, for example, (B1) specimen has almost a straight line while (A) and (B2) curves are concave, an opposite of an ideal photovoltaic i-v curve which should be convex and approaching a rectangular shape.

(2) Analysis

In Fig. 1., (B1), being a straight line and situated between a concave and an ideal convex curve, is consequently the better of the three types of specimen.

A drastic difference is the short circuit current: (B1) and (B2) have about 50 times higher value than (A), the overall efficiency is increased by about 30 times. This demonstrates most drastically the importance of the idea of using two types of organic semiconductor layers.

The appearance of the curve (B1) has a simple explanation: when a solar cell is shunted by a parallel resistor with resistivity value lower than that of the solar cell, the i-v curve gradually becomes linear when the resistivity is reduced. This situation is illustrated in Fig. 2, where a good silicon solar cell is shunted with resistors of various resistance. One cause of the shunt conductivity could be due to the inhomogeneity of the specimen and some TCNQ forms a short circuit linkage between the electrodes. One possible method to verify this mechanism is

to use a microscope with strong light source to delineate if there are separate TCNQ regions besides the intended (TCNQ) + (tetracene) region.

The explanation of the appearance of curves (A) and (B2) is more complex. We list two situations where such curves are observed: (1) In heavily radiation-damaged silicon solar cells of p or n configuration with lithium in the n-region, after the cessation of the radiation, instead of a spontaneous recovery as in the case of lightly radiation-damaged case, spontaneous damage is observed and the i-v curve in this case bears a similarity to that observed in the present case.²⁾ The cause was interpreted as due to a large reduction of the carrier generation center and a high concentration of the trapping center. But there is no direct experimental verification. (2) Another possibility is due to the inexistence of a strong junction to separate the positive and negative charge carriers into distinct regions, such as n- or p- regions in the ordinary silicon solar cells. This point will be discussed again in Section IV of this report.

III. Transient Photovoltaic Effect in Tetracene

While tetracene solar cell so far has not shown the utility of a photovoltaic energy conversion device, the effect of the reversal of photovoltaic current polarity as a function of the wavelength of the illuminated light is a rather novel phenomenon;³⁾ and it is conceivable to be of practical interest, for example,

for detection of optical informations. In order to proceed along this direction, one important aspect is to investigate the dynamic characteristics of the photovoltaic current. As will be discussed in Section IV, dynamic data also provides information which allows to separate the positive and the negative current, therefore to aid in the basic quantitative analysis.

(1) Experimental Arrangement

In our previous work, to measure the transient response, the light pulse was controlled directly by the electrical circuit switch. This arrangement gives a light pulse as shown in Fig. (3a). It has two undesirable aspects. First, the electrical signal from the switch already triggers the oscilloscope before the actual light signal appears. Second, the time to reach a steady state is about 200 nsec. To overcome this defect, we decided to leave the lamp in steady operation, and use a camera shutter to turn on or off the light. In this way, we have a light source nearer to a square pulse.^{3b)} The rise time is reduced to about 70 msec, and the transient response is triggered by the light signal. A silicon solar cell is used to detect the light signal. The response of this solar cell is less than 1 msec. In the measurement of organic solar cells, therefore, we will always use S_i solar cells to monitor the shape of light pulse as well as the light intensity.

The camera shutter is operated by an electrical solenoid operated on 120 volts a.c. source. We hope to replace it by a d.c. source in the future and, by adjusting the mechanical

spring, an improvement will be made on the shape and the duration of the pulse.

(2) Experimental Results

Fig. 4 shows two curves. Curve (a) is the reference signal obtained with Si cell. The shape is nearly rectangular in 2 sec/scale picture. Curve (b) is the terminal voltage, measured at 1 megohm shunt of the oscilloscope of a tetracene-TCNQ cell. The vertical scale is 0.05 V/scale. The light intensity, calibrated from curve (a), is about 110 mw/cm^2 . The effective area of the organic cell is slightly larger than 1 cm^2 .

At t_0 , the light is switched on and curve (a) reaches a steady state almost instantly. On the other hand, curve (b) reaches a maximum first, then slowly decays and reaches a steady state only after a time longer than 10 sec. The ratio between the maximum and the final value, just before the time marker t_1 , is less than $1/20$. That is, in a steady state operation, the photovoltaic voltage is only about one-twentieth of the maximum voltage obtainable from the organic cell.

Next, at t_1 , which is about 6 sec after the light is on, the light is turned off. Curve (a) returns to the zero level immediately. On the other hand, curve (b) first shows a sharp increasing spike, then decays at a time rate of about 0.5 sec. That is, there is a residual photovoltaic voltage even though there is no more light illumination. Furthermore, this residual voltage does not return to zero, instead, it becomes a signal with opposite polarity.

Fig. (5) shows two new effects. The vertical scale is the same as in Fig. 4, but the time scale now becomes 2 sec/scale. First, looking at the tail of curve (b) of Fig. 4, this curve, after crossing zero level, went to the opposite polarity. Fig. (5) shows this curve reaches a new maximum, and eventually decays to zero level in a time of about 10 sec.

Second, by comparing Figs. (4) and (5), we note that while the vertical magnitude of curve (a) remains constant, that of curve (b) has been decreased. This is especially prominent in the two maxima at the opposite sides of zero line. Thus, there is a sign of fatigue. This effect is shown in Fig. 6. Curve (0) is taken for a specimen which has been kept in the dark overnight. Curve (1) is taken at 20 sec after t_1 where the light is turned off. Curve (2) is taken at 20 sec after curve (1) is completed. The steady state signal of organic cell is the distance separated from o-line; the value is 0.02 volts. On the other hand, the value at maximum of curve (o) is estimated to be 0.5 volts.

The detailed structure of the maximum is shown in Fig. 7. As always, curve (a) refers to Si solar cell and curve (b) to organic solar cell. At t_0 , light is injected. From the time scale of .1 sec/scale, we can estimate the breadth of the peak. But the most interesting observation is that, using curve (a) as a reference, it is known that Si solar cell has a linear response to the light intensity. Therefore, curve (b) shows that the organic solar cell has non-linear response: at weak light (before the shutter is fully opened to reach a maximum light inten-

the sharp corner of curve (a)), curve (b) already shows a ...
within the accuracy of measurement, the maximum of curve (b)
seems to coincide with the maximum of the light intensity.

Our next measurement is to investigate the rate of the recovery of the decayed photovoltaic activities of Fig. 6. This is shown in Fig. 8. Following the descending order from the top, the first curve was taken after the organic solar cell is exposed to the light for a full two minutes. After that, light is turned off by the shutter for 5 sec. And then light is turned on again and this first curve is obtained. This curve has a barely noticeable maximum. After a one minute (time counted at the beginning of the light pulse) interruption, the second curve is taken. The consecutive curves correspond to 3 10 and 20 minutes. A datum is also taken at 60 minutes, although not shown in Fig. 8. The result is plotted in Fig. 9, curve (I). The curve (II) is for $1-V/V_m$, where V_m is an extrapolated value of V as the time approaches infinity. We took a value of $V_m=0.3$ volts and (II) is a reasonable good straight line. That means the recovery of follows first order kinetic with a recovery rate of 12.4 minutes.

All above measurements were made with 1 MΩ shunt of the oscilloscope. If a parallel 6K resistor is introduced, we obtain the result of Fig. 10. The vertical scale in this case is 0.005 volts. We see that photovoltaic current reaches a steady state much faster in comparison with the photovoltaic voltage data of Fig. 5. Otherwise, all the characteristics of Fig. 5 are preserved: the fast maximum, the spike as light is

turned off, and the reversal of the polarity after the light is turned off.

Our last experimental result, Fig. 11, is for the "pyrazine 101"-TCNQ cell. In the similarity aspect, (1) we observe the maximum, (2) when light is turned off, there is a spike, but somewhat less pronounced, (3) decay follows to zero as the light is turned off, and there is no reversal in the voltage. The most interesting difference is that the decay at repeated pulse still exists, but much less noticeably. The vertical scale for both reference Si cell and organic cells are the same as before, thus the maximum voltage in "pyrazine 101"-TCNQ is somewhat less than that of tetracene=TCNQ cell, but the decay after the maximum is very much reduced.

In conclusion, we observe a wealth of new phenomena as almost each figure in this report shows some unusual characteristics. During this period, some new publications have appeared which, although in different fields, are obviously interrelated with our work:

(1) One drastic difference in the solar cell structure of A. Glubovic used in this experiment is that the mixture type consists of two organic materials. An existence of interaction, either in the form of charge transfer or some new interaction process, is evident. Some of this aspect has been reported by Ishihara and Nakada on the anthracene-tetracene mixture.

(2) Queisser et al,⁵⁾ pointed out the importance of p-n junction structure in semiconductor where the dielectric relaxation time is larger than the carrier recombination lifetime.

Their experiment was performed on complex compensated gallium arsenide. It seems that the organic semiconductors fall automatically also into this category and a study in parallel to the work of Queisser et al. would be interesting.

(3) In organic semiconductors, the role of bulk and surface combination has not been clarified.⁶⁾ In this regard, the recent theoretical treatment of Silver et al.⁷⁾ and the calculation of Eer Nisse⁸⁾ is most interesting.

The experimental results suggest two conclusions: (1) a drastic change in the performance of the organic solar cells can be obtained, and (2) a defect structure is inherent in some organic semiconductors either as an intrinsic property or as a result of processing. The fact that an undesirable decay in tetracene-TCNQ is minimized by a substitution of "pyrazine 101" is most encouraging in this respect. (2) From the present data, as indicated in Figs. 6 and 9, one can separate the effect due to either photoionization of traps or surface recombination. This point will be discussed in the following section.

IV Spectral Response of Transient Photovoltaic Current

In a previous work³⁾ experimental results and theoretical analysis were presented concerning the dependence of the steady state photovoltaic current of tetracene on the wavelength of injected photons. Present work extends to the dynamic case where the time dependence at several selected wavelengths is investigated. The previous work has been emphasized on the transport

equation, and in the original version, two different lengths--one for optical absorption and attenuation, and the other for carrier diffusion--are introduced. There are some criticisms⁹⁾ and a considerable revision was made by changing the boundary conditions of the diffusion equation. Essentially the same results are obtained. This revised version is included in this report as an Appendix I.

In the subsequent work¹⁰⁾ we attempted to interpret the results by the same transport equation which was used in Ref. 3, extended to the time dependent case. The result was not successful: when we carried out numerical calculation, the transient response curve was found to be a monotonic curve to approach either a steady positive or a steady negative

state. This is not consistent with the experimental data which show a positive maximum, and the negative state is reached from an initially positive value.

From the above results we are led to an interpretation that the transient current is responsible for the simultaneous presence of a positive and a negative current. Therefore, an entirely different approach is used based on the superposition of two currents. The result, in the form of a complete paper, is presented in Appendix II. We draw here only one important result: according to our analysis, the photovoltaic current generated in tetracene is more than an order of magnitude of the observed steady state current which is the net difference of a positive and a negative current. The magnitude of the currents is

almost equal and the consequent net difference indeed is very small. Furthermore, by an examination of the literature⁶⁾ we conclude that this small difference is mainly due to the surface recombination and a photovoltaic process based on this effect would have a severe limitation on the photovoltaic efficiencies.

V Solar Cell Configurations

Two alterations of the presently adapted solar cell configuration are proposed in the following:

(1) The presently adapted configuration uses glass (quartz) substrate and electrodes and the organic material ~~are~~ evaporated on it. The photovoltaic efficiency is higher when light enters from the glass side of the solar cell. The explanation is an over-all optical index matching between air and the specimen. Another utility of glass substrate is to protect the Al electrode from atmospheric oxidation. It will not be conceivable that if the organic semiconductor device becomes practical, one still retains such a bulky and brittle structure.

We propose to use plastic substrate similar to that used in Cds solar cells. This will give flexibility and lighter weight. Since the plastic does not have a good uv transparency, the light will not enter through the plastic. Instead, a silicon oxide layer of sufficient thickness is evaporated on the top electrode. This will basically replace the functions of quartz glass. In the new system, therefore, both electrodes are protected. A configuration of protected electrodes has the

advantage that the thickness of the electrode could be considerably reduced and yet to have an equivalent conductivity of thicker ones, and an increase in the optical transparency.

(2) In the organic solar cell, net contributions to photovoltaic current are not the carriers generated deep in the materials far away from electrodes. This is caused by several factors-- by the higher concentration of traps, short diffusion lengths of minority carriers, and the inefficient charge separations. Therefore, in spite of the fact that a thicker specimen would absorb more photons and consequently create larger numbers of minority carriers, the observed net photovoltaic current is reduced. On the other hand, thinner specimen would waste the photons. We have done the following experiment: a complete tetracene solar cell is placed upon a second complete cell and the photovoltaic i-v curve of the second cell is measured. A still appreciable photovoltaic effect, corresponding to about 30% of the cell without being observed by the top solar cell (Fig.12) is observed. If one can improve the intimate contact between different layers and optimize the thickness of electrodes and the specimen, one should be able to introduce more layers of solar cells and improve the efficiency of conversion per unit area several times.

References

1. P. H. Fang, M. Hirata and M. Hirata, "Investigation of Organic Semiconductor for Photovoltaic Application", Final Report, AFCRL Contract F 19628-70-C-0263. 1 July, 1970-31 Oct., 1970.
2. P. H. Fang and Y. M. Liu, "Interaction of Lithium with Impurities and Defects in Silicon", Appl. Phys. Lett. 9, 364 (1966).
3. P. H. Fang, A. Glubovic and Noreen A. Dimond, "Photovoltaic current anomaly in tetracene" (Submitted for publication).
4. Y. Ishihara and I. Nakada, "On the energy gap of Anthracene" J. Phys. Soc. Japan 28, 667 (1970), also comments by J. Scvorakowshi, *ibid*, 29, 1390 (1970).
5. H. J. Queisser, H. C. Casey, Jr. and W. van Roosbroeck, "Carrier transport and potential distribution for a semiconductor p-n junction in the relaxation region," Phys. Rev. Lett. 26, 551 (1971).
6. N. Geacintov, M. Pope and H. Kallmann, "Photogeneration of charge carriers in tetracene," J. Chem. Phys. 45, 2639 (1966).
7. M. Silver, K. S. Dy and I. L. Huang, "Monte Carlo calculation of the transient photo-current in low-carrier-mobility materials," Phys. Rev. Lett. 27, 21 (1971).
8. E. P. Eer Nisse, "Accurate capacitance calculations for p-n junctions containing traps," Appl. Phys. Lett. 18, 183 (1971).
9. Reference of J. Chem. Phys.
10. P. H. Fang, First Quarterly Report (1971) of the present contract.

Contributing Personnel

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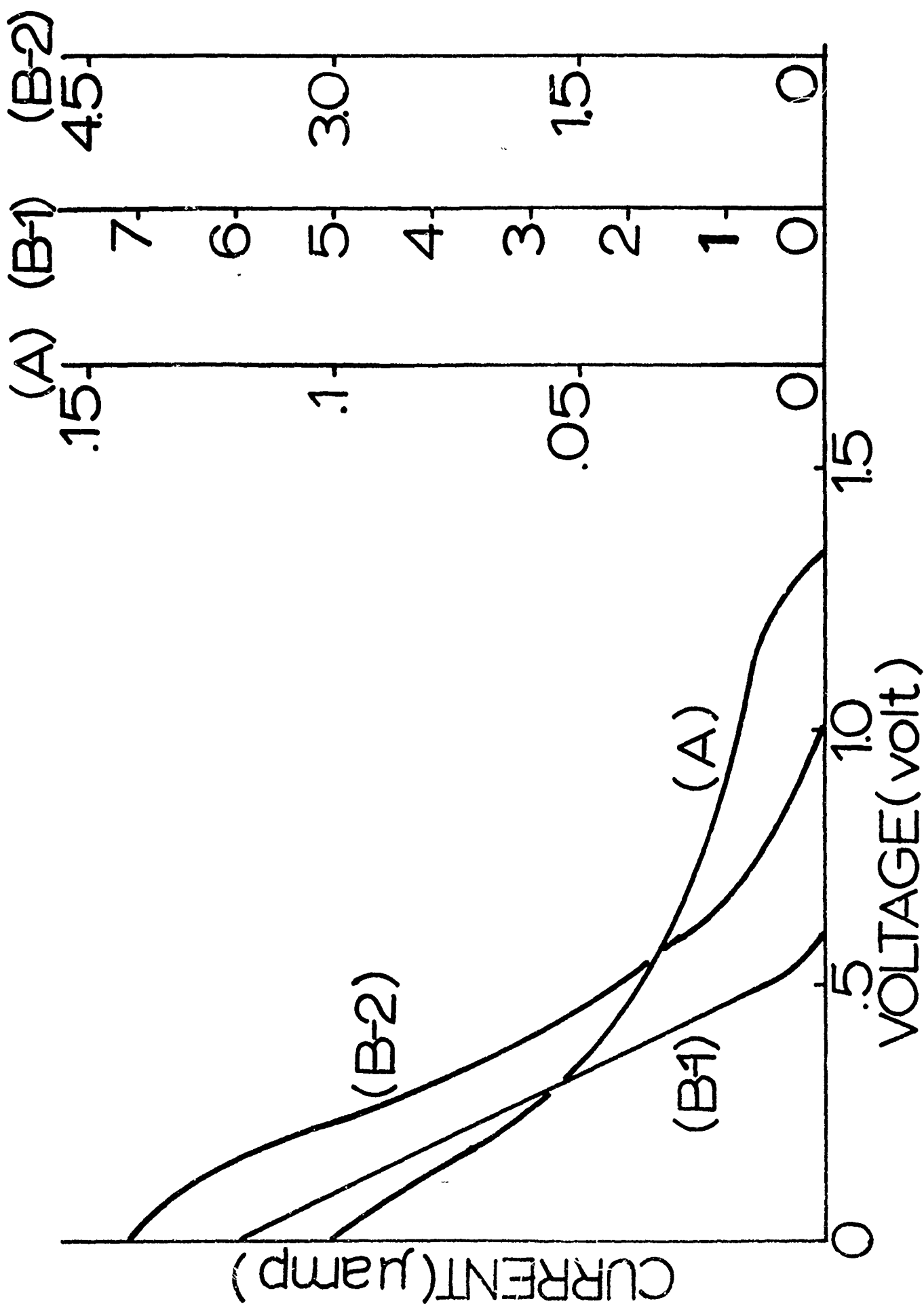


FIG.1

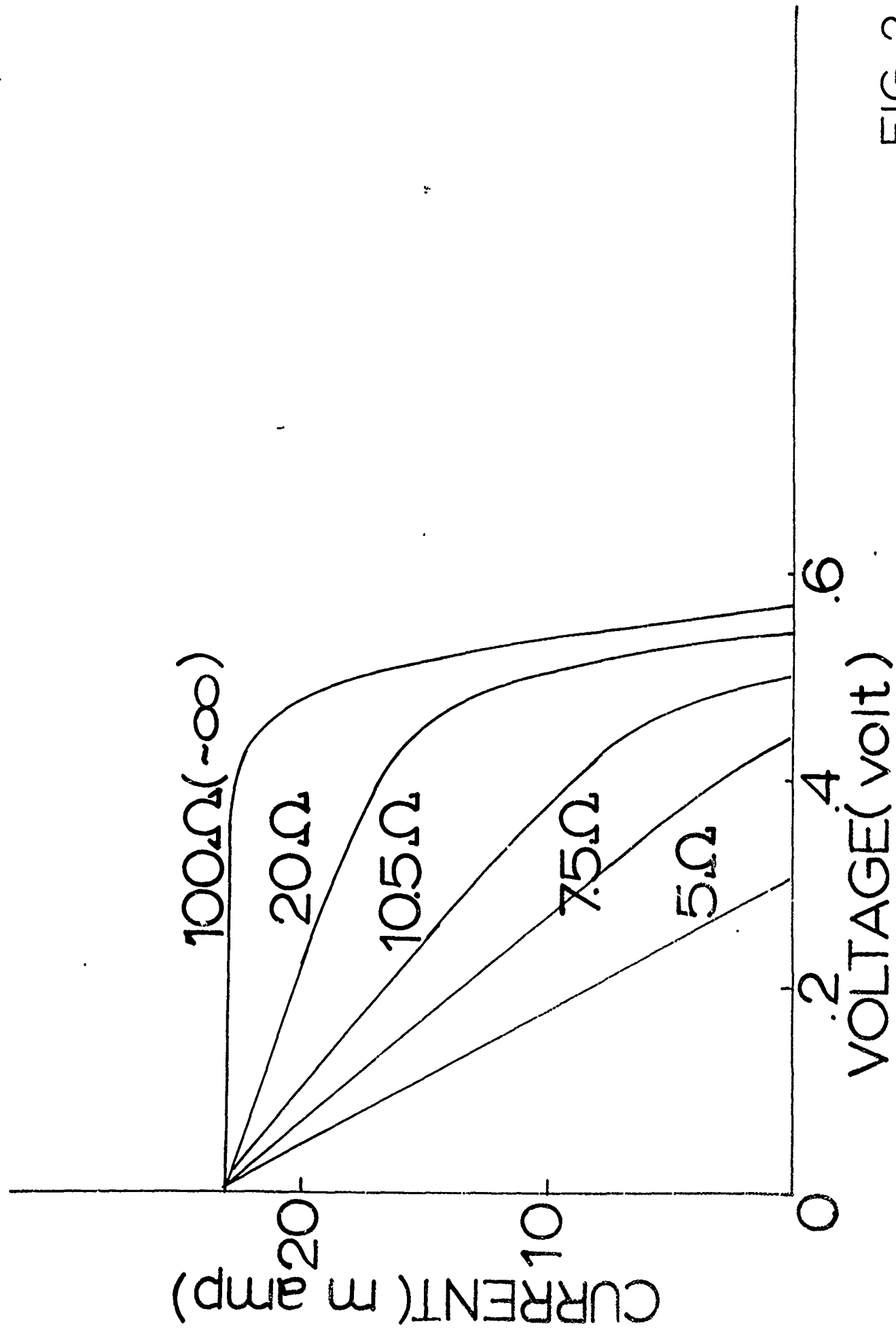
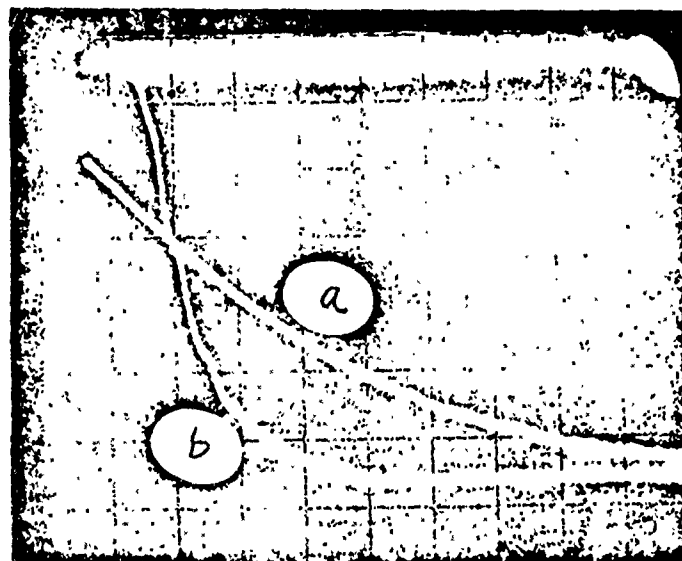


FIG. 2

FIG. 3



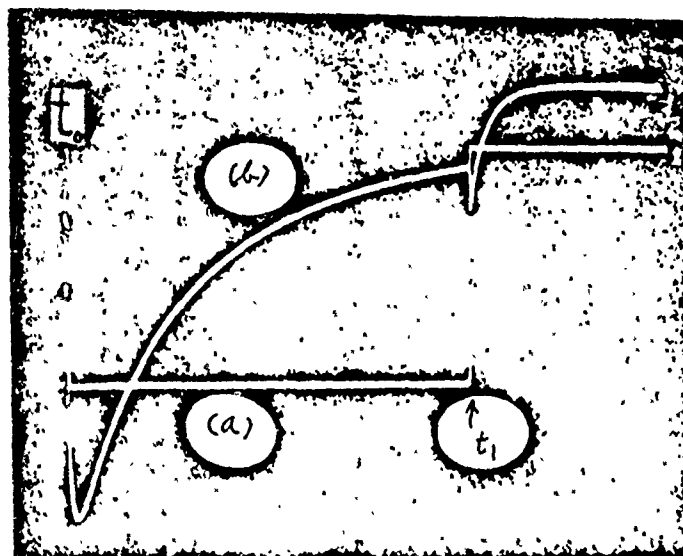
O (volt/scale)
↓

TIME(20msec./scale)

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18

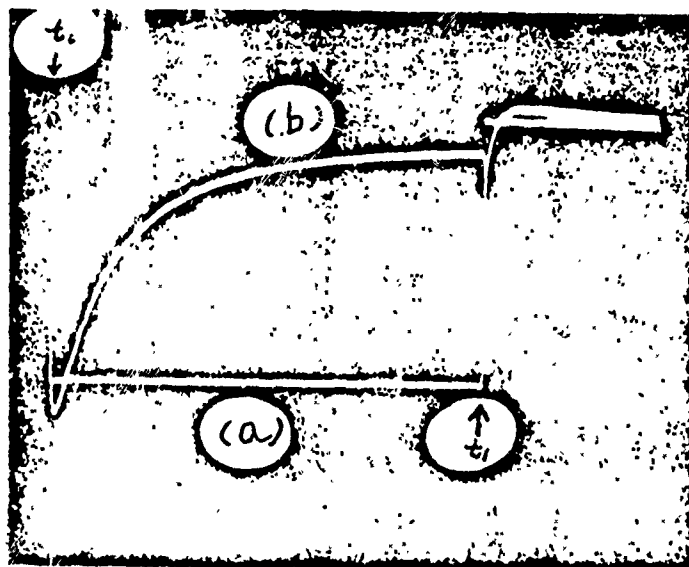
FIG. 4



O
↓

TIME(1 sec./scale)

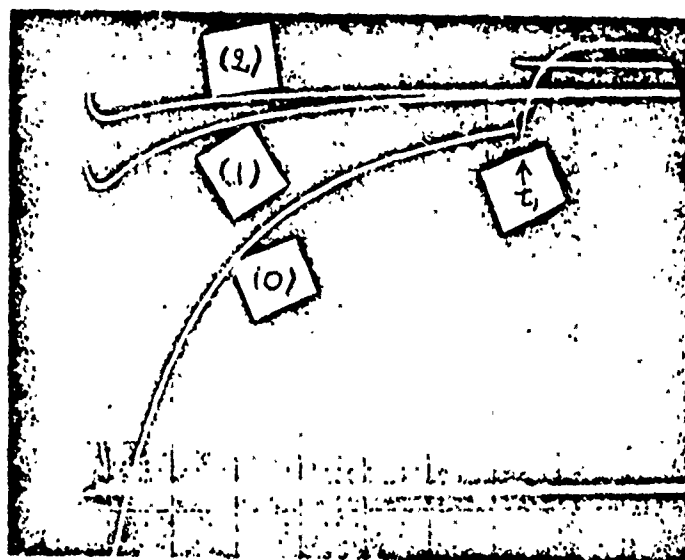
FIG. 5



TIME (2 sec./scale)

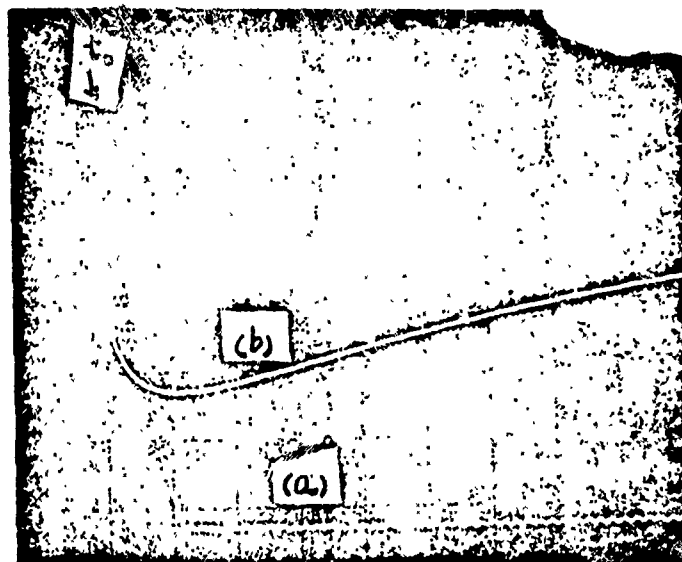
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FIG. 6



TIME (1 sec./scale)

FIG. 7



TIME(1 sec./scale)

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FIG. 8



TIME(2 sec./scale)

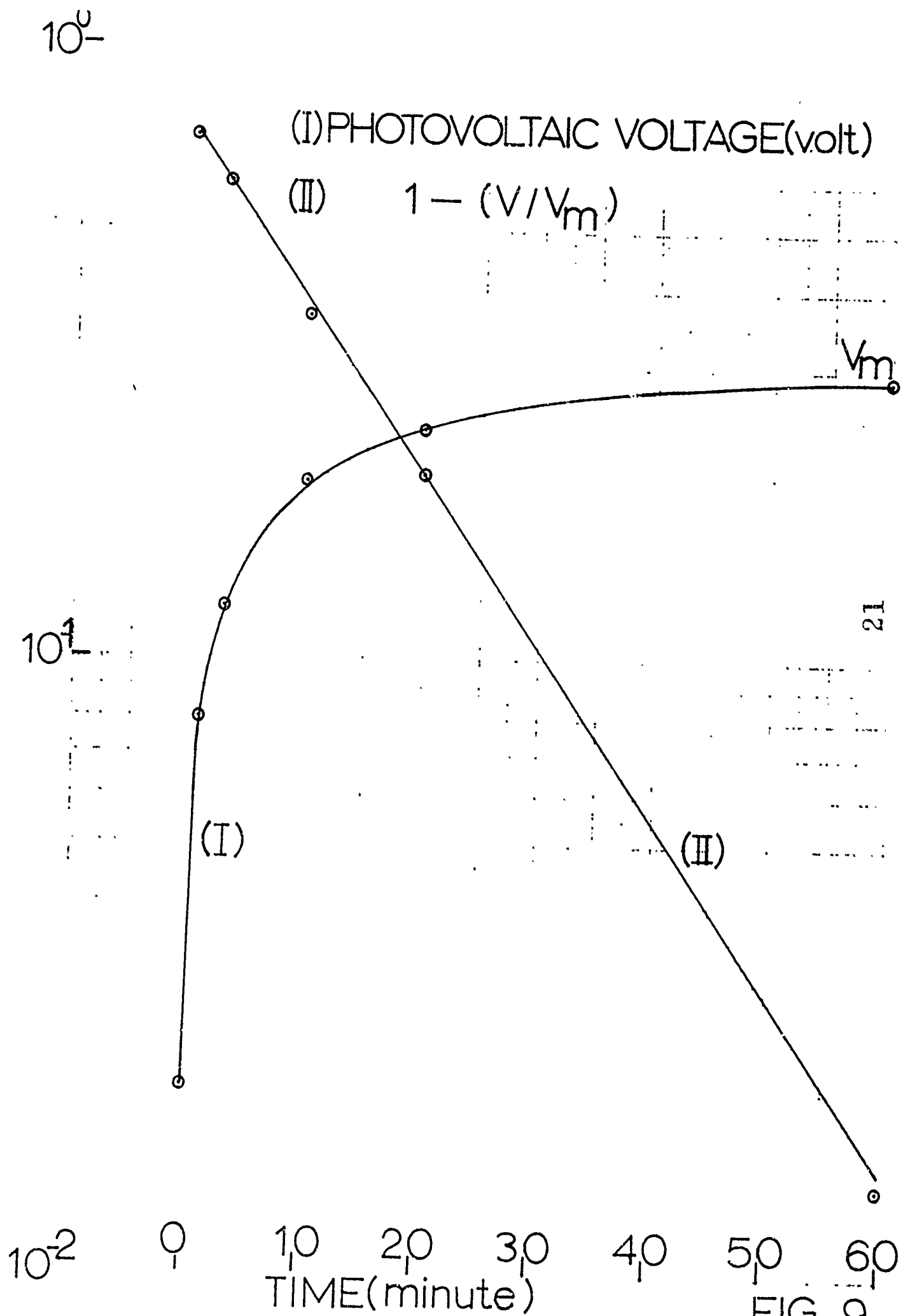
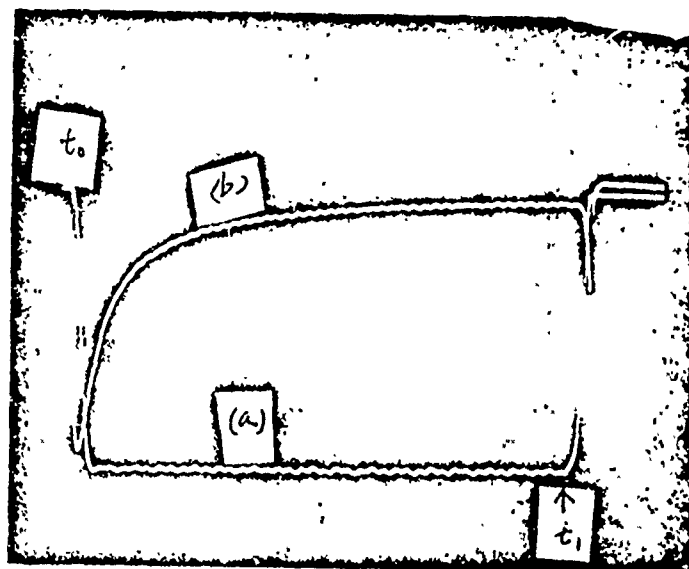


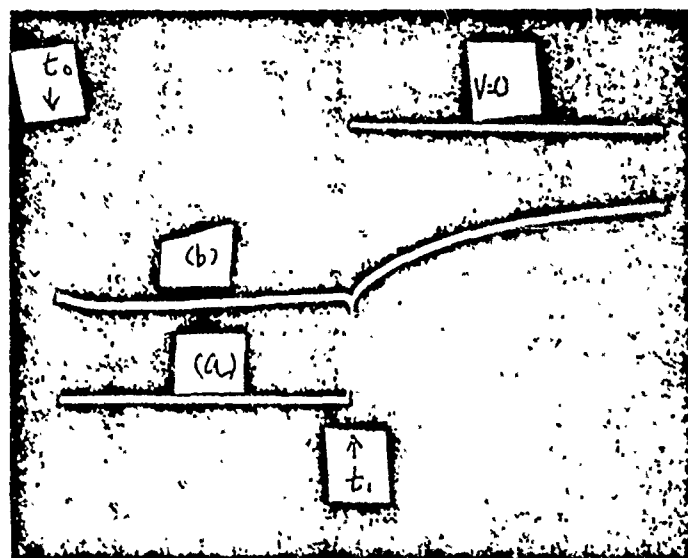
FIG. 9

FIG. 10



TIME(.1 sec./scale)

FIG. 11



TIME(.5 sec./scale)

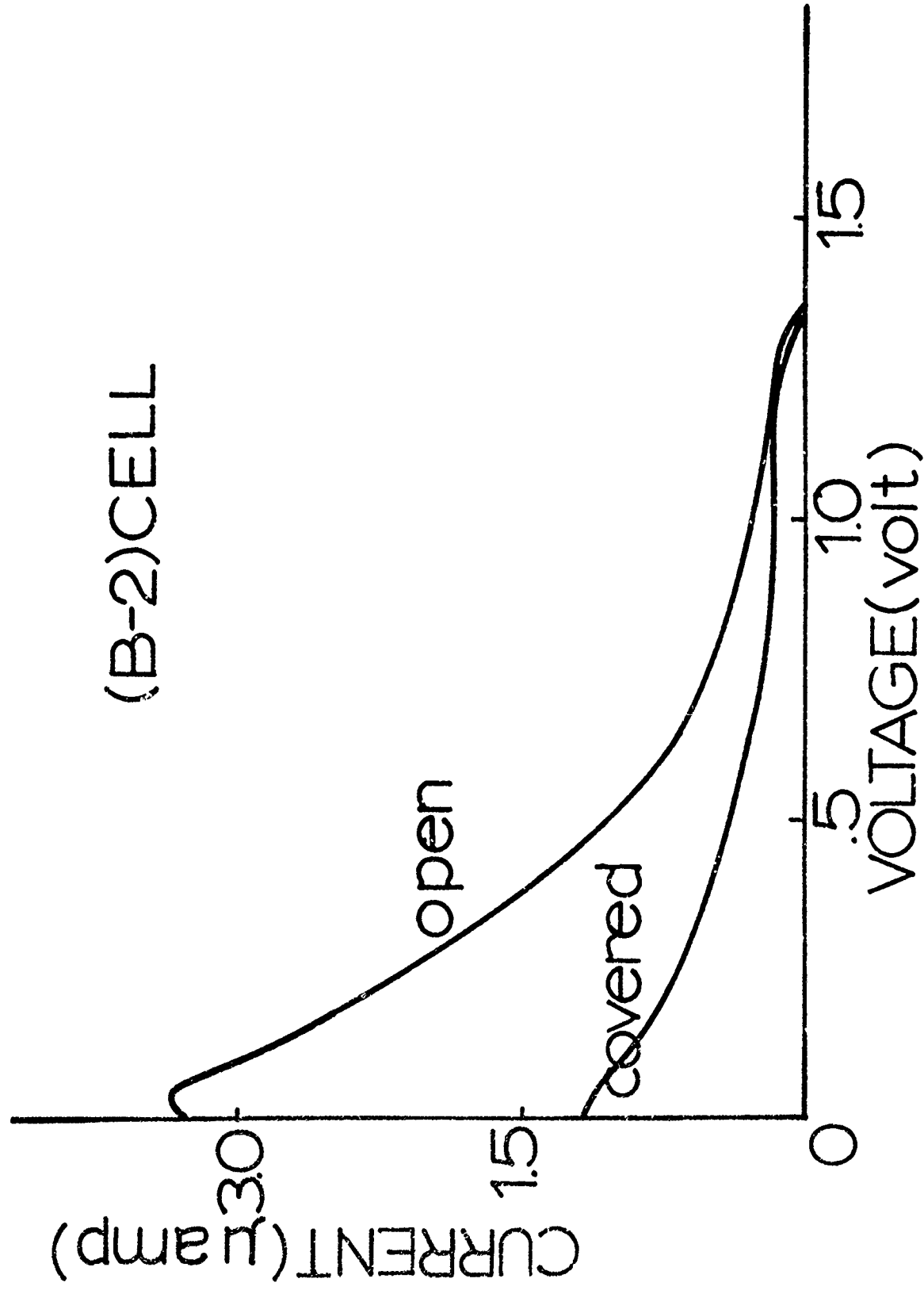


FIG.12

Appendix I
Photovoltaic Current Anomaly in Tetracene

Photovoltaic Current Anomaly in Tetracene*

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Abstract

A reversal of the polarity of photovoltaic current in tetracene at some wavelength region is observed. This effect is interpreted as the consequence of the photovoltaic transport equation. The observational data implies that either there is a very large surface recombination rate, or the major annihilation of the excitons instead of on the surface in the interior of the crystal.

I. Introduction

In this paper, we would like to analyze the wavelength dependence of the photovoltaic current observed in tetracene, an organic semiconductor. Our particular interest is an observation that at a certain wavelength region, the polarity of the photovoltaic current is reversed, as shown in Fig. 1. We propose to explain this phenomenon by a diffusion equation employed by Geacintov, Pope and Kallmann (GPK)¹⁾ in the investigation of similar material. However, in the work of GPK, some approximations are used which we will show to be not valid, and their result does not show a reversal of the polarity in the whole wavelength region.

The specimen of tetracene for the photovoltaic experiment consists of a thin layer ($\sim 1\mu$) of tetracene sandwiched between two semi-optically transparent and electrically conductive film of gold electrodes.²⁾ Monochromatic light from a grating spectrometer is projected to a strip of about 2 mm width of the specimen of approximately $1 \times 1 \text{ cm}^2$ in dimension. In view of a somewhat similar observation in ZnS due to partial illumination of the specimen,³⁾ we have also tried to have light projected on the complete specimen and we found in our case, the result is independent of the area coverage of the illumination.

II. Transport Equation

We would like to investigate the spectral dependence of the photovoltaic current, especially in the reversal of the polarity

of the photovoltaic current. In the work of GPK, origins of this current are explained in terms of different excited states in tetracene, and the surface trapping effect. It is important to recognize that the polarity of the photovoltaic current is not only dependent on the sign of the charge carriers, but also on the direction of the charge flow between the electrodes. In fact, we propose that this reversal has a natural explanation in the transport equation. The fact that the diffusion current could have positive as well as negative signs does not seem to be recognized in the literature¹⁾ and in the following we will discuss this problem.

Under a steady state, the equation of photovoltaic carrier, n , can be written, ^{1,4)}

$$D \frac{d^2 n}{dx^2} - \frac{1}{\tau} n = -\epsilon I_0 e^{-\epsilon x}, \quad (1)$$

where D is the diffusion coefficient and τ is the lifetime of the carrier in tetracene, ϵ is the optical absorption coefficient of tetracene, x is the distance travelled by the carrier to the site of collection, and I_0 is the light intensity at the surface of tetracene where light enters, and I_0 is dependent on the wavelength λ . In our experiment, constant energy, instead of constant number of photons, is used for I_0 . Since the experiment is carried out in a continuous but confined wavelength region of 0.3 to 0.6 μ , we do not expect a great difference in the spectral response curves.

Since the diffusion length $l = \sqrt{D\tau}$, with $x = l\xi$, $\epsilon l = \beta$, Eq. (1) becomes,

$$\frac{d^2n}{d\xi^2} - n = -\frac{\tau}{\ell} I_0 \beta e^{-\beta\xi}. \quad (2)$$

A particular solution of n is that

$$n_p = \frac{\tau I_0 \beta}{\ell(1-\beta^2)} e^{-\beta\xi}. \quad (3)$$

For the general solution, from the homogeneous part of Eq. (2), we have,

$$n_1 = a_1 e^{\xi} + a_2 e^{-\xi} \quad (4)$$

therefore,

$$n = n_1 + n_p. \quad (5)$$

The coefficients a_1 and a_2 are determined from the two following boundary conditions: In the surface recombination, with a surface recombination velocity k ,

$$kn(0) = \frac{D}{\ell} \left[\frac{dn}{d\xi} \right]_{\xi} = 0. \quad (6)$$

The optical density of the specimen is ϵd , where d is the thickness of the specimen. Since our specimen is polycrystal with multiple grain boundaries, there is a spatial distribution of distance where the recombination and capture takes place. Therefore, we have two different coordinates for . In optical transmission and absorption,

$$\begin{aligned} \epsilon d &= \epsilon \ell \frac{d}{\ell} \\ &= \beta \xi_1, \end{aligned} \quad (7)$$

on the other hand, ξ in Eq. (4) becomes independent of $x=d$, $\xi \rightarrow \xi_2$ with

$$\eta = \xi_2 / \xi_1 < 1, \quad (8)$$

and the second boundary condition is that

$$a_1 e^{\eta \xi_1} + a_2 e^{-\eta \xi_1} + \frac{\tau I_0 \beta}{\ell(1-\beta^2)} e^{-\beta \xi_1} = 0 \quad (9)$$

From Eqs. (6) and (9), we can solve for a_1 and a_2 , and the final solution for $n(o)$ is now,

$$n(o) = I_{o\ell} \frac{\tau}{\ell - \beta^2} (\cosh \eta \xi_1 - e^{-\beta \xi_1} - \beta \sinh \eta \xi_1) / (\alpha \sinh \eta \xi_1 + \cosh \eta \xi_1) \quad (10)$$

where $\alpha = k\ell/D$.⁵⁾

The photovoltaic current, which is our central interest, is obtained from Eq. (10) with a simple multiplier constant,

$$i = e \frac{\ell}{\tau} \left. \frac{d\mu}{d\xi} \right|_{\xi=0} = e \gamma k n(o), \quad (11)$$

where γ is the fraction of photovoltaic carriers collected and e is the electronic charge.

When ξ_1 and $\beta \xi_1 \gg 1$, $n(o)$ becomes approximately,

$$n(o) = I_{o\ell} \frac{\tau}{\ell(1+\alpha)} \frac{\beta}{1+\beta}. \quad (12)$$

This is the same equation given by GPK. Since $\beta > 0$, $n(o)$ is always positive and in this case, the polarity of the photovoltaic current would not have a reversal for all β , therefore, for the whole wavelength range. We will see later that $\beta \xi_1$ is not necessary $\gg 1$ for some wavelength regions, and in these regions the polarity of the photovoltaic current in fact shows a reversal.

III. Analysis of Experiment

Fig. 1 shows the spectral response of the photovoltaic current of specimen with three thicknesses. In the case of thick specimens, photovoltaic current bears a resemblance to the absorption spectrum (Fig. 2). When crystal becomes thinner, in

the spectral regions where the optical density has minima, the polarity of i changes from positive to negative and to positive again.

Fig. 2 gives the spectrum of ρ for three specimen thicknesses. We should note that, while in the inorganic semiconductors for photovoltaic application, there is only a single transition to the major absorption, in the organic semiconductor as in the present case, there are several major absorption peaks corresponding to multiple transition processes.

From Eq. (10), for given values of ξ and η we can calculate $n(o)$ as a function of ρ . The values of ρ are based on the experimental data of Fig. 2 which relates ρ to the wavelength λ . Therefore, $n(o)$, consequently, the photovoltaic current i , as a function of λ is obtained. Fig. 3 is the result where the numerical value of the parameters are,

$$\begin{aligned} e k \gamma \tau I_0 / \ell &= 7.8 \times 10^{-9}, \\ \eta &= .30, \\ \xi_1 &= d / \ell = 6 \times 10^{-5} \text{ cm} = 3 \\ \beta \xi_1 &= 2.303 \rho \end{aligned} \quad (13)$$

These parameters are determined in the following manner:

The value of ℓ is given by GPK. Therefore, for given d , ξ_1 is determined, and from given ϵ , β is determined. The only remaining parameter is η . We observed from Figs. 1 and 2 that at 4650 Å, $i=0$ and $\rho=1.8$. The only way for Eq. (10) to become zero is that

$$\cosh \eta \xi_1 - e^{-\beta \xi_1} - \beta \sinh \eta \xi_1 = 0. \quad (14)$$

Substituting for the values of β and ξ_1 , a value of 0.30 is obtained for η .

The general agreement between the theoretical curve and the experimental data, over several decades of logarithmic scale, is

remarkably satisfactory. Appreciable differences occur in the two ends of the spectrum, and the two negative peaks on each side. One source of deviations could be contributed by the experimental limitations: the theoretical calculation is based on the monochromatic wavelength. In the experiment, the grating has a finite dispersion and the specimen always sees a band of wavelengths; consequently, β does not have a single value at each point along the curves of Fig. (1) and (2).

Another conceivable source of deviations is that in a more exact description, ξ' and η should have ranges of values and each has a distribution in the range. However, to reformulate our problem by taking into account the distribution functions, it will unduly complicate the mathematical problem without yielding additional physical insights. Therefore, we have decided not to expand our work in this direction.

We believe our theoretical interpretation proposed in this paper is not confined to tetracene since the result is a direct consequence of the solution of a general transport equation for photovoltaic carrier generation. Therefore, similar observation of the reversal of the polarity of the photovoltaic current is expected in silicon. In this case, since the diffusion length is in the order of 0.05 to .2 cm,⁴⁾ at the wavelength near the absorption edge where the absorption coefficient ϵ becomes compatible with the reciprocal of the diffusion length, this anomaly should be observed.

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References

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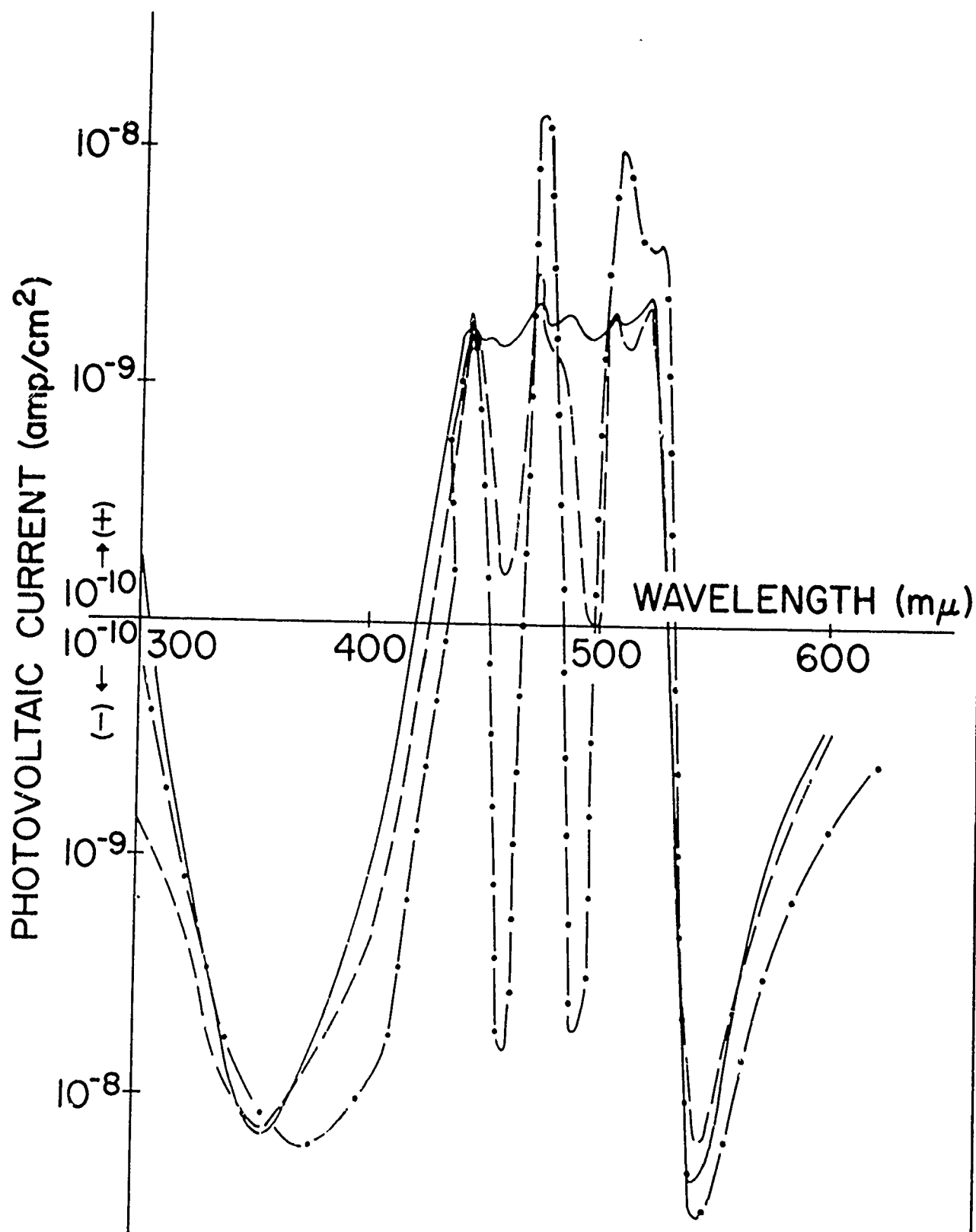
1. N. Geacintov, M. Pope and H. Kallmann, J. Chem. Phys. 45, 2639 (1966).
2. A. Górubovic, Organic Photovoltaic Devices, Proc. OAR Res. Appl. Conference March, 1967
3. O. Cheroff and S. P. Keller, Phys. Rev. III, 98 (1958).
4. R. L. Cummerow, Phys. Rev. 95, 16 (1964).
5. An essentially similar result can be obtained by a system consisting of layers of different crystals, but the analytical result is very complicated and is not presented here.

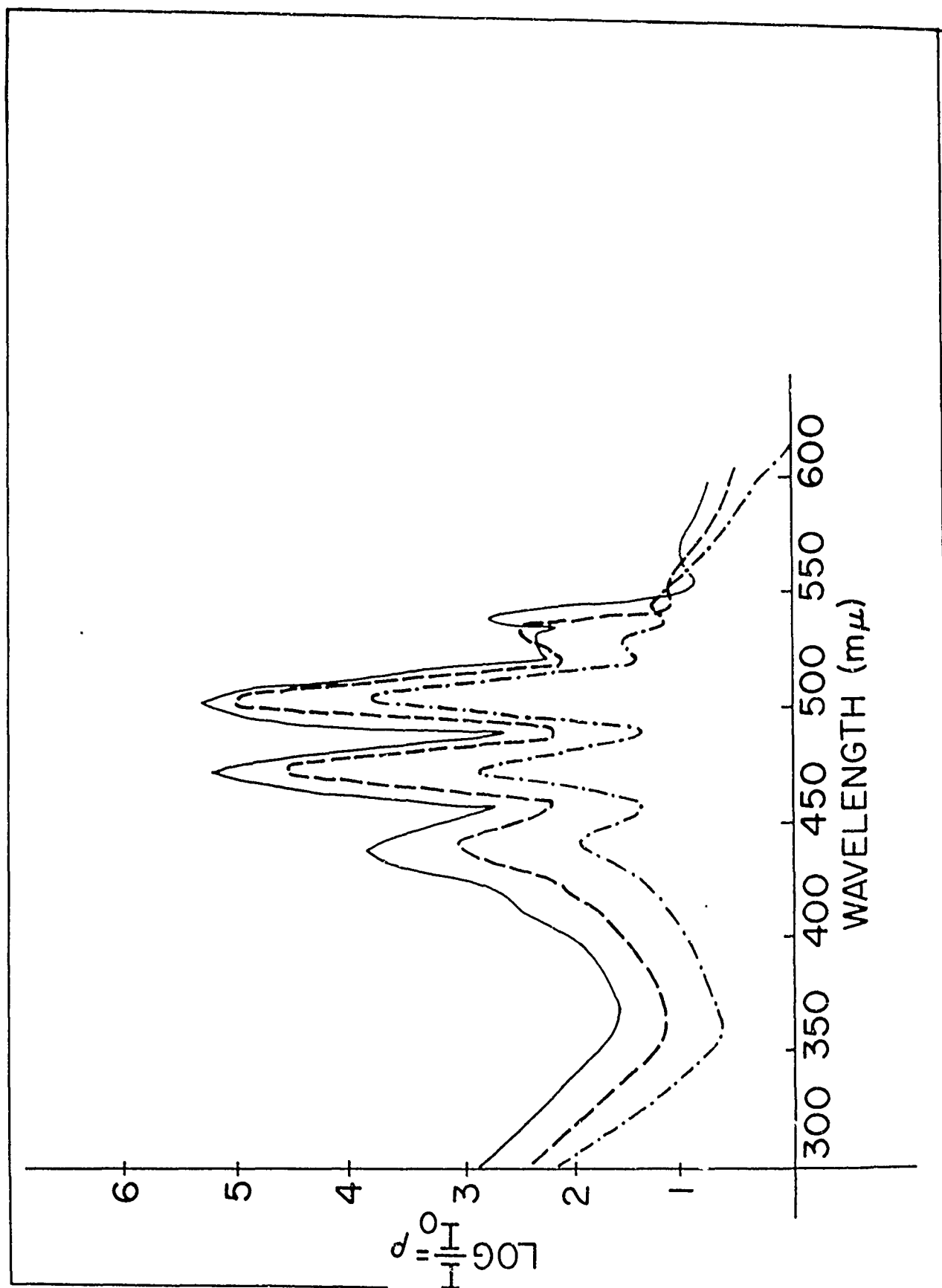
Illustrations

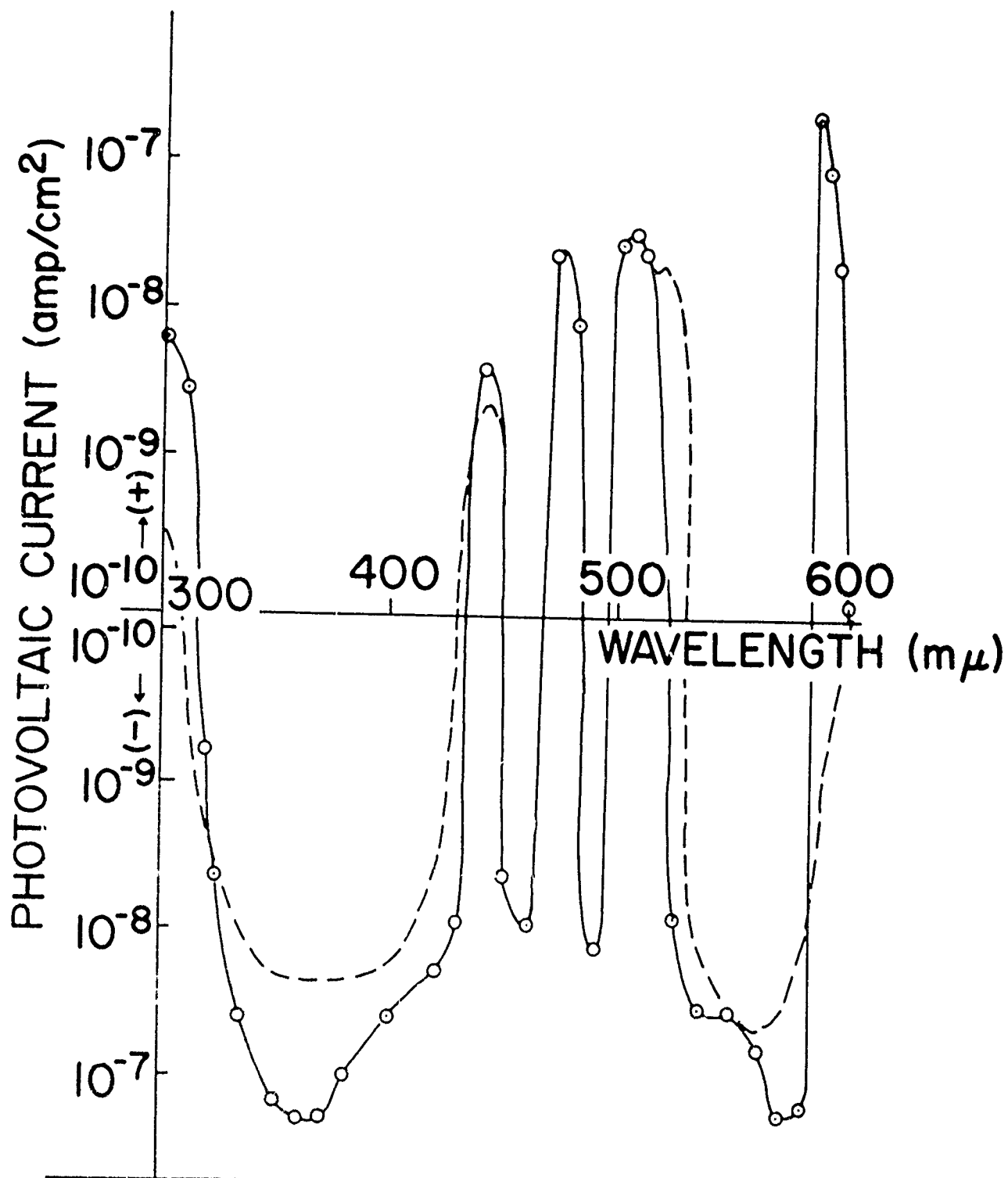
Fig. 1. Spectral response of the photovoltaic current of tetracene of different thickness; (---), 0.6μ ; (---), 1.0μ ; (___), 1.6μ .

Fig. 2. Optical density of tetracene specimen of Fig. 1, with some thickness designation.

Fig. 3. Spectral response of photovoltaic current:
(---), experimental data of tetracene of 0.6μ thick;
(-o-), theoretical result from Eq. (5) and (6) with numerical parameters given in the text.







Appendix II

Transient Photovoltaic Current in Tetracene

Transient Photovoltaic Current in Tetracene

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Abstract

In order to analyze the positive and negative charge current in the organic semiconductor, tetracene, we measured the transient photovoltaic current. From the rate equations for the relaxation of these two currents, the magnitude and the relaxation time of these currents are evaluated. The magnitude of the steady state value of these two currents are almost equal, and they are more than one order of magnitude larger than their net difference. This difference is the usual photovoltaic current referred to in the characterization of the photovoltaic efficiency of tetracene.

I. Introduction

In a previous paper by Fang, Golubovic and Dimond (FGD)¹⁾, we presented experimental results and theoretical analysis of the dependence of the steady state photovoltaic current in tetracene on the wavelength of injected photons. The present work extends to the transient case where the time dependence is also investigated. In the previous work, we found the polarity of the photovoltaic current is dependent on the energy of the excitation photons. In the present work, we would like to investigate the same dependence for the transient photovoltaic current. Reucroft, Kronick and Hillman²⁾ have reported some anomalous behavior of this current. Their time scale is rather coarse (in the unit of minutes). We have observed down to a fraction of a second. We will show that the result at the region of fraction of a second gives most direct information on the composition of these currents.

In this paper, in Section II, we would like to present the experimental results. In Section III, theoretical analysis based on the superposition of one positive component and one negative component of the photovoltaic current is made. This model is based on the experimental observation of the non-linear dependence of the photoconductivity on the light intensity³⁾, and the non-symmetry of the rise and the decay when a pulsed light is used for the excitations.⁴⁾

II. Experimental Results

The specimen configuration has been described in the work of FGD. The transient photovoltaic current is recorded by an x-y recorder with x on time base, and y-import is triggered by the fast light signal. The rise time of this signal is 70 msec. The result is given in Fig. 1.

When light is injected to the specimen, through different band pass filters, there is a finite relaxation time for response and the photovoltaic current reaches a maximum in the order of 0.2 sec. After this over-shooting, there is a gradual decrease. This decrease follows one of two courses depending on the wavelength of the injected photon: either to reach a stable value with the same polarity as the initial response current, or a continuous decrease goes to the opposite polarity before a stable value is reached. In a closer examination, we found that these two courses are closely related to the photovoltaic anomaly:¹⁾ with our arrangement which assigns negative polarity on the side of electrode where light is illuminated, we found that in the case of positive current, there is no reversal in the polarity of the transient photovoltaic current; in the case of negative current, there is a reversal. Fig. 1 shows two curves; in the curve with 5000\AA (100\AA band width) illumination, there is no alteration of the polarity. In the case of $3100\text{-}4000\text{\AA}$ illumination, obviously, the current polarity is reversed. Although in the case of short wavelength, the bandwidth of the filter is 900\AA , our light source does not have appreciable emission at wavelength

shorter than 3500\AA . Therefore, effectively, the wavelength in this case is $4200 \pm 200\text{\AA}$.

In comparison of those two curves, we also noted that the relaxation time to reach saturation in the case where there is no polarity reversal is faster. This characterization is true for all wavelengths although the result is not presented here.

III. Two Component Model

In a study of the light intensity dependence of the photoconductivity current, Golubovic and Dimond⁴⁾ observed that, under pulsed light excitation, the rise time is faster than the decay time, and the decay follows a second order kinetics. The implication is that there are two relaxation times in the operative. From the characteristic of the transient photovoltaic current as shown in Fig. 1, it is implied mathematically that these two relaxation processes have opposite polarities. Therefore, the transient current is analyzed with one component which follows the first order kinetics and another component which follows one second order kinetics. The relative sign of those two components is determined, in the present work, from the fitting of the experimental data by the proposed model; that is,

$$i(t) = i_1(t) + i_2(t), \quad (1)$$

where the transient current $i_1(t)$ and $i_2(t)$ are given by Eqs. (A6) and (A6) in the Appendix, respectively. Eqs. (1) has four unknown parameters, αI , τ , βI and k , which are to be determined from the experimental data. To evaluate these parameters,

instead of a more complicated least square approach, we simply selected four arbitrary data points from which the values are found. The result is given in the following table:

<u>wavelength</u>	<u>$\alpha I\tau$</u>	<u>τ (sec)</u>	<u>$\beta I/k$</u>	<u>$(2\beta I k)^{-1}$ (sec)</u>	<u>$i(t=\infty)$</u>
4200Å	-133.7	.139	+128.7	.0785	-5
5200Å	-36.1	.151	+39.1	.0910	+3

The units of $\alpha I\tau$ and $\beta I/k$ have the same arbitrary unit as in Fig. 1 and of $i(t=\infty)$: i.e., the steady state value of i in the above table.

Substituting the values of parameters of the above table to Eq. (1), $i(t)$ can be computed for different values of t , and the result is shown in Fig. 1. The fit is generally satisfactory, except at some intermediate time intervals. An improvement can be made in the fitting by using mixed first and second order kinetics as discussed in the photo-induced current in polyvinylcarbazole⁵⁾ or by a different combination of reaction kinetics. However, we found that there is no basic alteration of the values of the preceding table.

Several points are noted from the table:

(1) The current component following the first order kinetics is negative, and the component following the second order kinetics is positive.

(2) The difference in the relaxation time of the negative component at the two wavelengths is 6%. Within the accuracy of evaluation, this difference is practically null. The difference

in the case of positive component cannot be made because of a difficulty in calibrating the light intensity values at present.

(3) The magnitude of the two components, that is, the value of αI_r and $\beta I/k$ are, for a given wavelength, practically the same.

(4) From a practical point of view, the steady state current, because of (3), is more than an order of magnitude smaller than that of individual component. This effect evidently is a major cause for the smallness of the photovoltaic efficiency observed in tetracene.

IV. Discussion

A basic photovoltaic problem of the organic semiconductor is the origin of the positive charge current and the negative charge current. There are several experimental observations and qualitative descriptions. Since, in the experimental data as illustrated in the present paper, these currents occur simultaneously, a quantitative method to evaluate these two currents separately, as described in the present work, would be useful.

Frankevich and Balabanov found that gold, for example, forms a good hole injection contact and exhibits negative potential.⁶⁾ However, when gold is used for both electrodes, the gold electrode deposited on the glass substrate forms positive potential relative to the gold electrode deposited on the semiconductor.⁴⁾ These currents are also affected by the energy of photons: since there is no evidence of multiple carrier generation, this effect is interpreted as due to the strength of the absorption coefficient.

In a weak absorption case, a photoionization of trapped electrons gives a negative current. In the case of strong absorption, excitons are recombined near the surface and a positive current is resulted.^{7,8)} This origin of this effect must be different from that observed by Golubovic and Dimond; in the case of gold electrodes on both sides of the semiconductor, independent of the side of light injection, the gold electrode deposited on the semiconductor is always negative. Finally, Geacintov et al.⁹⁾ discussed a negative current which is independent of the electrodes and depends only on the absorption coefficient at specific values of photon energy where transitions to excited states are observed.

From the result of the present work, we conclude on two grounds that the process of Geacintov et al.⁹⁾ is dominant in tetracene: (1) for a given wavelength, the magnitude of the positive and the negative currents are almost equal, therefore, the current carriers are dominantly generated in the bulk and (2) the small difference of these two currents, which gives the steady state current as observed in most experiments, is originated at the side of surface recombination, therefore, a small effect due to the electrode is observed.

In conclusion, transient current measurements provide a method to evaluate quantitatively the opposite charge current observed in tetracene, and similar methods should be useful in the investigation of other organic semiconductors. By repeated transient measurements at specific time intervals, we have also observed a change in the transient current. From the data, one can measure quantitatively the photoionization of trapped

charges. This problem is currently under investigation.

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Appendix

We present here the kinetic equation of first and second order kinetics, for a pulsed light and a continuous light injection separately.

For a pulsed light, only the decay is observed, and the kinetic equation is,

$$\frac{di_1}{dt} = -\frac{i_1}{\tau} \quad (A-1)$$

for the first order kinetics, and

$$\frac{di_2}{dt} = -k^2 v_2^2 \quad (A-2)$$

for the second order kinetics. With i_0 as the initial current, i.e., the current at the value of $i(t)$ when the light pulse is dropped to zero, we have, for Eq. A-1,

$$i_1 = i_0 e^{-t/\tau} \quad (A-3)$$

For Eq. (2),

$$i_2 = i_0 / (1 + k^2 i_0 t) \quad (A-4)$$

Therefore, for i_1 , the relaxation time is independent of the light intensity; for i_2 , the relaxation time depends on the light intensity as well as on the pulse length where i_0 is reached.

In the case of continuous light injection, a source term should be included. Thus,

$$\begin{aligned} \frac{di_1}{dt} &= -\frac{i_1}{\tau} & \text{for } t < 0 \\ &= -\frac{i_1}{\tau} + \alpha I & \text{for } t > 0 \end{aligned} \quad (A-5)$$

where I is the light intensity and α is the current generation

rate. The solution of (A-5) is that, with the initial condition $i=0$ at $t \leq 0$, i.e. at $I=0$,

$$i_1 = \alpha I \tau (1 - e^{-t/\tau}). \quad (A-6)$$

For second order kinetics,

$$\begin{aligned} \frac{di_2}{dt} &= -k^2 i_2^2 && \text{for } t < 0, \\ &= -k^2 i_2^2 + \beta^2 I^2 && \text{for } t > 0, \end{aligned} \quad (A-7)$$

with the same initial condition as (A-5)

$$i_2 = \frac{\beta I}{k} \left[1 - \frac{2}{1 + \exp(2\beta I k t)} \right] \quad (A-8)$$

We note that, while the relaxation function and the relaxation time of (A-6) are the same as those of the pulsed decay case, those of (A-8) are different from those of (A-4). Furthermore, qualitatively, in the pulsed case, the decay rate of second order kinetics is slower than that of the first order case. The opposite is the result for the case of continuous injection.

Finally, the transient current, $i(t)$, of two component models is the sum of (A-6) and (A-8).

List of Figures

Fig. 1. Transient photovoltaic current of tetracene. The curves are experimental data, the points are calculated from Eq. (1).

References

1. P. H. Fang, A. Golubovic and N. A. Dimond, "Photovoltaic Current Anomaly in Tetracene (submitted for publication).
2. P. J. Rencraft, P. L. Kronick and E. E. Hillman, Mol. Cryst. and Liquid Cryst. 6, 247 (1969).
3. N. Almeleh and S. E. Harrison, J. Phys. Chem. Solids, 26, 1571 (1965).
4. A. Golubovic and N. Dimond (to be published)
5. J. E. Carnes and P. J. Warter, Phys. Rev. 5 B 1557 (1972).
6. E. L. Frankevich and E. I. Balabanov, Phys. Stat. Sol. 14, 523 (1966).
7. L. E. Lyons and O. M. G. Newman, Aust. J. Chem. 24, 13 (1971).
8. V. V. Vladimirov, M. V. Kurik and O. Yu. P. Piryatinskii, Dokl. Akad. Nauk SSSR, 181, 1365 (1968) (Transl. Soviet Phys. Dokl. 13, 739, 1969).
9. N. Geacintov, M. Pope and H. Kallamnn, J. Chem. Phys. 45, 2639 (1966).

